

**CHEMICAL AND BIOLOGICAL SYSTEMS
FOR REGENERATING ACTIVATED CARBON
CONTAMINATED WITH HIGH EXPLOSIVES**

**John P. Knezovich
Jeffrey I. Daniels
Michael K. Stenstrom
Harro M. Heilman**

This paper was prepared for submittal to the
Proceedings Demil '94
Luxembourg, Luxembourg
November 14-16, 1994

December 1994



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

CHEMICAL AND BIOLOGICAL SYSTEMS FOR REGENERATING ACTIVATED CARBON
CONTAMINATED WITH HIGH EXPLOSIVES

John P. Knezovich, Ph.D., and Jeffrey I. Daniels, D.Env.
Health and Ecological Assessment Division, L-453
Lawrence Livermore National Laboratory
Livermore, California 94550
(Voice: 510-422-0925 and 510-422-0910; FAX: 510-423-6785;
Electronic mail: knezovich1@llnl.gov and daniels1@llnl.gov)

Michael K. Stenstrom, Ph.D., P.E., and Harro M. Heilmann, Dipl.-Ing.
Civil and Environmental Engineering Department
University of California
Los Angeles, California 90024
(Voice: 310-825-1408 or 310-825-3335; FAX: 310-206-5476;
Electronic mail: senstro@seas.ucla.edu)

ABSTRACT

Activated carbon has been used as a substrate for efficiently removing high explosives (HEs) from aqueous and gaseous waste streams. Carbon that is saturated with HEs, however, constitutes a solid waste and is currently being stored because appropriate technologies for its treatment are not available. Because conventional treatment strategies (i.e., incineration, open burning) are not safe or will not be in compliance with future regulations, new and cost-effective methods are required for the elimination of this solid waste. Furthermore, because the purchase of activated carbon and its disposal after loading with HEs will be expensive, an ideal treatment method would result in the regeneration of the carbon thereby permitting its reuse. Coupling chemical and biological treatment systems, such as those described below, will effectively meet these technical requirements.

The successful completion of this project will result in the creation of engineered commercial systems that will present safe and efficient methods for reducing the quantities of HE-laden activated carbon wastes that are currently in storage or are generated as a result of demilitarization activities. Biological treatment of hazardous wastes is desirable because the biodegradation process ultimately leads to the mineralization (e.g., conversion to carbon dioxide, nitrogen gas, and water) of parent compounds and has favorable public acceptance. These methods will also be cost-effective because they will not require large expenditures of energy and will permit the reuse of the activated carbon. Accordingly, this technology will have broad applications in the private sector and will be a prime candidate for technology transfer.

INTRODUCTION

Research and development activities involving high explosive (HE) compounds at federal facilities, including U.S. Department of Defense (DoD) ammunition plants and Department of Energy (DOE) laboratories, have resulted in the contamination of soils and ground waters.^{1,2} Environmental laws and regulations now in place require remedial actions and controls to remove such contamination or to treat it to levels that are safe for the environment and public health. Furthermore, regulations currently under consideration are likely to impose stricter cleanup criteria (i.e., from ppm to ppb levels³) and to restrict or prohibit open burning/open detonation (OB/OD) of HE wastes. Although activated carbon can be used to effectively meet these wastewater cleanup

criteria, HE-laden activated carbon is itself a listed hazardous waste⁴ and technologies for its treatment are not available.

Biological treatment processes are attractive because they can result in the complete destruction of hazardous compounds. However, conventional biological treatment processes suffer from a general lack of reliability, especially when used in the degradation of hazardous compounds. For example, intermittent changes in the concentration of the hazardous constituents in a waste stream makes the maintenance of a continuously acclimated culture for the biological degradation of such substances very difficult. We have addressed these problems and are in the process of implementing a novel biological system for the treatment of HE compounds that are initially sorbed on activated carbon.^{5,6}

TECHNICAL APPROACH

Overview of Approach

The approach that we have adopted will provide flexible options for the treatment of HE-contaminated waste water and HE-laden activated carbon. The use of activated carbon as a pretreatment step is attractive because it permits maximum efficiency for wastewater cleanup and can be readily coupled to biological treatment, which accomplishes waste destruction. Because the use of activated carbon as a treatment for the removal of HE from aqueous-waste streams has been well established, we have focused our efforts on developing systems for the biological treatment of waste water and the regeneration of HE-laden activated carbon. The adsorption, solvent/thermal desorption, and biological treatment steps of the process have been defined and feasibility testing for the hydrolytic regeneration of activated carbon also has been performed. The main thrust of this work, however, was the design and construction of a pilot-scale treatment system that could be used to test and demonstrate these approaches. This system, which was constructed and has been installed at the U.S. DOE Pantex Plant in Amarillo, Texas, can be readily adapted for the treatment of waste water and the activated carbon that is currently in use or being stored as hazardous waste at U.S. DOE and DoD facilities.

Adsorption and Desorption of HE From Activated Carbon

Two types of activated carbon are being used in our studies. The first is a relatively low-grade carbon (ABG-30) that has a mean particle diameter of 1.6 mm, a total surface area of 1,000 m²/g (as determined by BET analysis) and is commonly used for wastewater treatment. The second carbon, Filtrasorb-400, has a mean particle diameter of 0.65 mm and a total surface area of 950 m²/g (BET). Because we have found that the Filtrasorb-400 carbon has a very high efficiency and loading capacity (i.e., up to 40% by weight) for the removal of RDX and HMX from aqueous solution, we selected it for use in our pilot-scale treatment system (see below). Recovery of RDX and HMX from this carbon has been possible by treating it with a solution of ethanol and water (50/50; v/v) at elevated temperatures (i.e., > 70 °C). Carbon thus treated can be reused to remove HE from aqueous-waste streams. In addition to these studies, Dr. Stan Caulder of the Naval Surface Warfare Center (Indian Head, Maryland) is performing surface-

area and surface-chemistry analyses to determine the effects of multiple regenerations on the physical and chemical properties of activated carbon.

The feasibility of using base hydrolysis as an initial treatment for the removal and destruction of HEs sorbed to activated carbon was also assessed and has produced very promising results. Because this approach has not yet been integrated into our overall treatment scheme, however, the results of this work are presented at the end of this report and we are continuing to pursue this process in fiscal year (FY) 1995.

Development of a Biological Treatment System

Although HEs are generally refractory to biological degradation, microorganisms are present in the environment that have the ability to degrade these compounds.^{7,8,9} In addition, there is evidence that microorganisms that have been chronically exposed to HE compounds are "optimized" metabolically to perform this degradation.¹⁰ Based on this evidence, we found and acclimated for the degradation of HMX and RDX a consortium (i.e., a mixture) of microorganisms that could be maintained in biological reactors.

Because a wide diversity of microorganisms probably is required to carry out the HE-mineralization process, microbial populations obtained from different sources were used to develop the consortium for the treatment of HEs. The first source was located at the Lawrence Livermore National Laboratory's Site 300 high-explosive testing facility. Microorganisms were acquired from a lagoon that had historically received process waters from HE formulation and machining operations.¹¹ The second source of microorganisms was obtained from a Publicly Owned Treatment Works (POTW) in Los Angeles, CA (Hyperion Water-Treatment Plant), which is designed to treat municipal sewage and waste waters. In a POTW, contaminants are removed from water by direct microbial degradation or adsorption onto biological flocs that are subsequently removed in secondary clarifiers. These systems are effective because microbial degradation of organic compounds is mediated by enzymes of broad specificity, which are induced by structurally-related compounds. The populations of microorganisms present in a POTW, therefore, are robust and can be readily optimized for the treatment of waste water containing a variety of organic compounds.¹²

Both sources of microorganisms were mixed together and maintained in batch reactors that received mineral nutrient solutions supplemented with low concentrations (e.g., ≤ 5 mg/L) of HMX and/or RDX. The degradation of parent compounds as well as the appearance of degradation products was monitored by high-performance-liquid-chromatography (HPLC). This approach was used to identify the nutrient solution that would provide an optimal environment for the degradation of the HE compounds (see below).

The consortium of microorganisms that was ultimately selected for use in the treatment of HE was found to require a cosubstrate as a carbon and energy source in order to sustain microbial growth and HE transformation. Although many carbon sources can provide sufficient energy for microbial growth and metabolism, they do not equally support HE degradation (Fig. 1). For this reason, ethanol was selected as the cosubstrate of choice because it produced superior results for the degradation of RDX and HMX. Concentrations of ethanol that do not exceed 25 g/L were found to provide optimum degradation of RDX and

HMX, while ethanol in excess of 25 g/L was toxic to the microbial consortium. In addition to the requirement of a cosubstrate, the microbial consortium requires nitrate as an electron acceptor and several trace nutrients to support growth (Table 1). The presence of nitrate is critical because the consortium can neither grow nor degrade HE without it. The denitrifying function of this consortium is beneficial to waste treatment as it results in the removal of nitrate and nitrite, which are potentially hazardous byproducts, and produces nitrogen gas, which is benign. In addition, carbon-14 labeled RDX was used to verify that this consortium is capable of mineralizing this compound as evidenced by the production of carbon-14 labeled carbon dioxide.

The denitrifying consortium was subsequently used to define process conditions for the treatment of an HE-contaminated waste stream. Laboratory-bench scale columns were used to develop fixed-bed bioreactors that held immobilized microorganisms. These columns, which were approximately 50 cm in length and 1 cm in diameter, were filled with small silicone cylinders that provided surface area for the immobilization of microorganisms. Following the establishment of microbial biomass, these columns were operated in a flow-through mode for the treatment of HE. Following the successful treatment of RDX and HMX, pilot-scale columns were designed for the coupled treatment system (see below).

Treatment-System Design

In the system that was developed (Fig. 2), HE-contaminated wastewater is treated first by activated-carbon adsorption columns, which effectively remove the high explosive from the waste stream. Heated water and solvent are then recirculated through the exhausted columns to regenerate them. The HE-laden fluid is treated using the denitrifying consortium of microorganisms, which uses the ethanol as a carbon source and converts the HE to less hazardous end products. Based on this design, a pilot-scale treatment system was constructed and is currently undergoing evaluation at the U.S. DOE Pantex Plant in Amarillo, Texas. This system consists of 2-m \times 0.1-m glass columns that have been filled with either activated carbon (Filtrisorb-400) or with plastic saddles for supporting microbial growth. Two biological columns have been inoculated with the denitrifying consortium by introducing seed obtained from the laboratory-bench scale columns. The system was subsequently allowed to establish biomass by running it with nutrients and HMX and RDX (see Table 1) in a recirculating mode at low rates of flow (e.g., 1 L/h). The carbon column is currently being used to treat HMX-laden waste water and will undergo regeneration after it is loaded.

The pilot-scale treatment system has undergone an initial series of tests for determining its ability to degrade HE compounds. In these tests, the system was operated in a once-through mode with RDX and HMX added to the influent stream. Ethanol and micronutrients were also added to the influent to support organism growth and HE degradation. The biological system efficiently removed the HE compounds from solution as evidenced by their absence in the effluent stream (Fig. 3). Analysis of the off-gas from the biological column has revealed that the system is in fact operating in a denitrifying mode as evidenced by the presence of nitrogen gas (N_2) and the lack of nitrous oxide (N_2O) (Table 2). Analyses are currently underway to identify the presence of organic byproducts in the aqueous effluent.

The demonstration and testing of the coupled activated carbon/biological treatment system is currently in process. The activated carbon column that is being loaded with HMX is approaching saturation and will be used to demonstrate the feasibility of this approach for carbon regeneration. This column will be regenerated via solvent (ethanol)/thermal (80 °C) desorption and the recovered HE will be treated in the bioreactor.

Regeneration of Activated Carbon via Base Hydrolysis

Although base hydrolysis has been known to degrade HE compounds for quite some time¹³, it has received renewed attention as a method for destroying bulk HE. In this process, a caustic solution (e.g., pH \geq 12) is used to degrade compounds such as RDX and HMX to smaller molecular weight products via hydrolysis.¹⁴ Using this approach, we investigated the feasibility of using base hydrolysis for regenerating HE-laden activated carbon. Initial experiments were conducted to define the kinetics of RDX and HMX hydrolysis in dilute aqueous solution. The results of these experiments indicate that hydrolysis occurs rapidly and proceeds via a second-order rate constant at a temperature between 50 and 80 °C (Fig. 4).

The regeneration of RDX-laden activated carbon (ABG-30) via base hydrolysis was performed a total six of consecutive times on the same batch of carbon with no detectable loss of sorptive capacity (Fig. 5). Companion studies using carbon-14 labeled RDX verified that removal of this HE was complete following a two-hour treatment at 80 °C. The results of these studies confirm that base hydrolysis should be an effective approach for regenerating HE-laden activated carbon. Preliminary results for the subsequent biological polishing (e.g., treatment) of the hydrolysate by the denitrifying consortium that is being used in the pilot-scale treatment system (see above) are encouraging and indicate that these microorganisms can tolerate greater than ten-percent solutions of the HE hydrolysate. Experiments are in progress to define the ability of this system to remove potentially hazardous hydrolysate byproducts (e.g., formate and nitrite).

CONCLUSIONS

We have successfully demonstrated the individual components required for the production of an integrated system for the treatment of HE-laden waste water and HE-laden activated carbon. Such coupled chemical and biological treatment systems are attractive due to their relatively simple operation, inherent adaptability, and favorable economics. In addition, biological treatment enjoys a high degree of public acceptance. Accordingly, there are efforts within the U.S. DoD/DOE complex and in industry to develop such processes for the treatment of hazardous-organic compounds, particularly inventories of HE. In addition, because our system permits the reuse rather than disposal of activated carbon, waste minimization also is achieved and associated costs are reduced substantially. Work in progress is focused on demonstrating the operation of our coupled system on waste forms generated within the U.S. DOE/DoD weapons complex.

Our work complements existing research in this area, which includes the efforts of the U.S. Army to develop composting processes for the treatment of HE-contaminated soils, and the efforts at the Los Alamos National Laboratory (LANL) to develop base-hydrolysis methods for treating bulk HE directly. We are in close contact with the researchers at LANL so that we can mutually benefit from our complementary projects,

particularly those experiments advancing our understanding of the base hydrolysis of energetic materials.

The successful application of this technology will reduce the risk to the environment and the public by eliminating HE residues that otherwise could contaminate surface soils and ground water. This will be accomplished because the biodegradation process leads to the mineralization (e.g., conversion to carbon dioxide, nitrogen gas, and water) of parent hazardous compounds. Furthermore, this research will yield a waste-treatment technology that can be readily modified for the biological destruction of other HE compounds of interest to U.S. DoD facilities (e.g. Comp B, etc.), as well as for those compounds currently under development and potentially will have broad applications in the private sector.

ACKNOWLEDGMENTS

The technical assistance provided by Mr. Philip Goodfellow and Mr. Will Desmare of the U.S. DOE Pantex Plant, Amarillo, TX, and Dr. Stan Caulder of the Naval Surface Warfare Center, Indian Head, MD, are greatly appreciated. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

REFERENCES

1. Crow, N., R. Elwood, and P. Webster-Scholten (1986), *Distribution of High Explosives Compounds in Soil and Water at the 806/807 Lagoons, HE Process Area, LLNL, Site 300*, Lawrence Livermore National Laboratory, Livermore, CA, UCAR-10169.
2. Layton, D.W., T.E. McKone, C.H. Hall, M.A. Nelson, and Y.E. Ricker (1986), *Demilitarization of Conventional Ordnance: Priorities for Data-Base Assessments of Environmental Contaminants*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-15902, AD A182922.
3. Etnier, E.L. (1989), "Water Quality Criteria for Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)," *Regulat. Toxicol. Pharmacol.* **9**, 147-157.
4. U.S. Environmental Protection Agency (USEPA) (1993), *Code of Federal Regulations: 40 CFR Part 261—Identification and Listing of Hazardous Waste*, U.S. Government Printing Office, Washington, DC (1993), Subpart A, Section 261.3; Subpart C, Sections 261.20 through 261.24; and Subpart D, Section 261.32.
5. Knezovich, J.P., J.I. Daniels, M.K. Stenstrom, and P. Goodfellow (1993), "A Novel Biological System for Eliminating High Explosives in Wastewater," in *Abstracts of the Department of Energy Defense Programs Pollution Prevention and Integrated Technologies Workshop, Santa Fe, NM, October 1993*, U.S. Department of Energy, Washington, DC, p. 62.
6. Knezovich, J.P., J.I. Daniels, M.K. Stenstrom, and P. Goodfellow (1993), "A Novel Biological System for Regenerating Activated Organic Carbon Contaminated with High Explosives," in *Agenda and Abstracts for Waster Minimization/Pollution Prevention Conference IX*, San Francisco, CA, April 13-15, 1993, Waste

Minimization Division, Office of Environmental Restoration and Waste Management, U.S. Department of Energy, Washington, DC, p. 41.

7. Knezovich, J.P., and J.I. Daniels (1991), "Biodegradation of HE," *Water Environ. Tech.* **3**(3), 34.
8. McCormick, N.G., J.H. Cornell, and A.M. Kaplan (1981), "Biodegradation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine," *Appl. Environ. Microbiol.* **5**, 817-823.
9. Sikka, H.C., S. Banerjee, E.J. Pack, and H.T. Appleton (1980), *Environmental Fate of RDX and TNT. Final Report*, U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD, TR 81-538.
10. Spanggord, R.J., T. Mill, T.W. Chou, J.H. Mabey, J.H. Smith, and S. Lee (1980), *Environmental Fate Studies on Certain Munition Wastewater Constituents: Final Report, Phase II - Laboratory Studies*, SRI International, Menlo Park, CA, LSU-79034, AD-A099256.
11. Raber, E. (1983), *Chemical and Hydrogeological Evaluation of High-Explosive Process Wastewater Discharges at Site 300*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-19753.
12. Stenstrom, M.K., L. Cardinal, and J. Libra (1988), "Treatment of Hazardous Substances in Conventional Biological Treatment Plants," in *Proceedings of the AIChE Spring National Meeting*, New Orleans, LA, March, 1988, American Institute of Chemical Engineers (AIChE), New York City, NY.
13. Clear, A.J., and W.H. Rinkenbach (1945), *Procedures for Decomposing Waste High Explosives*, Picatinny Arsenal, NJ, Technical Report Serial N°. 1556, Defense Technical Information Center (DTIC), Alexandria, VA, Accession N°. AD 495569.
14. Spontarelli, T., G.A. Buntain, J.A. Sanchez, and T.M. Benzinger (1993), "Destruction of Waste Energetic Materials Using Base Hydrolysis," in *Proceedings of the 1993 Incineration Conference: Thermal Treatment of Radioactive, Hazardous Chemical, Mixed, Energetic, Chemical Weapon, and Medical Wastes*, Knoxville, TN, May 3 to 7, 1993, M.E. Wacks, Ed., Department of Environmental Health and Safety, University of California at Irvine (UCI), Irvine, CA, 1993 *Incineration Conference Proceedings*, pp. 787-791.

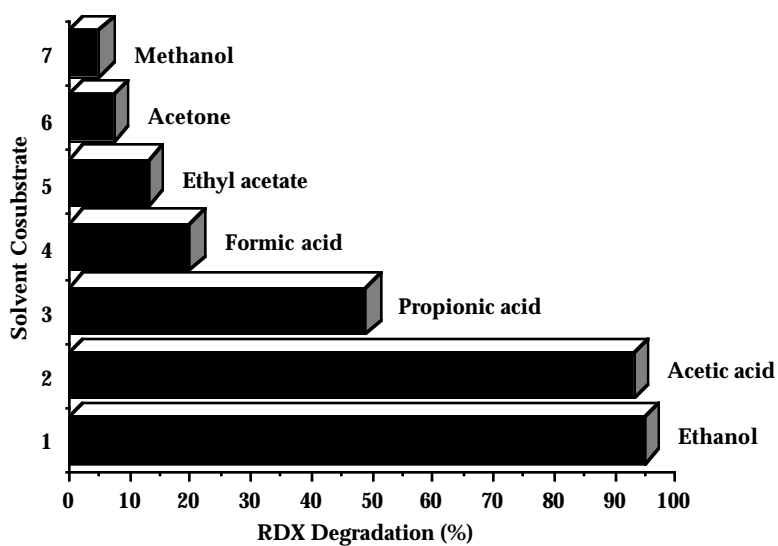


Figure 1. The influence of cosubstrate selection on the degradation of RDX.

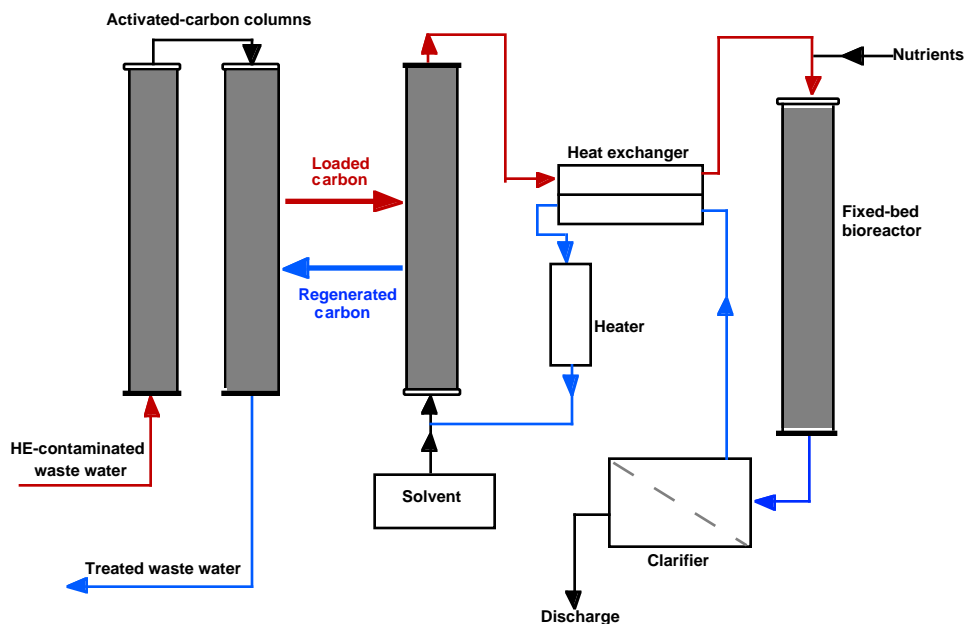


Figure 2. Diagram of the coupled chemical/biological treatment system that was designed to regenerate HE-laden activated carbon. In the initial step, activated carbon columns are used to remove HE from the wastewater stream. When the first column reaches HE break-through it is switched over to the solvent-thermal treatment that desorbs the HE, which is subsequently degraded in the fixed-bed bioreactor column.

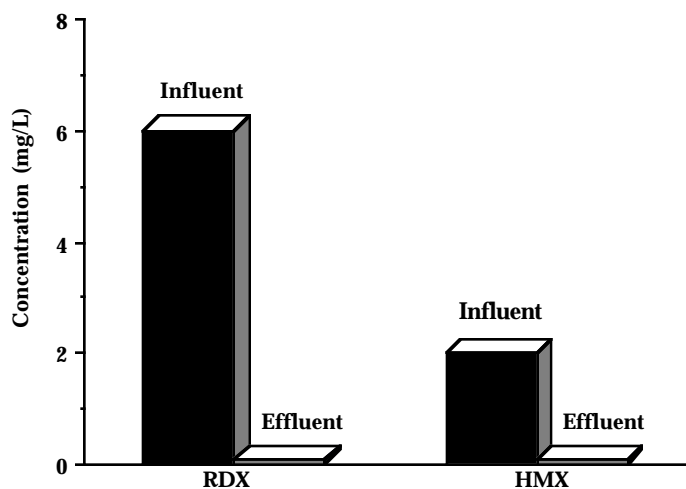


Figure 3. Results of RDX and HMX treatment studies conducted in the pilot-scale biological system. Neither compound was detected in the effluent stream (limit of detection is approximately 80 $\mu\text{g/L}$).

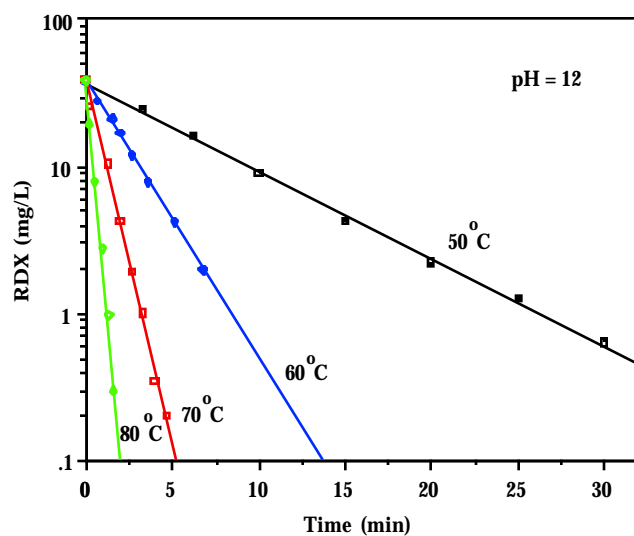


Figure 4. The influence of temperature on the kinetics of RDX hydrolysis in a solution of sodium hydroxide (20 mMol/L).

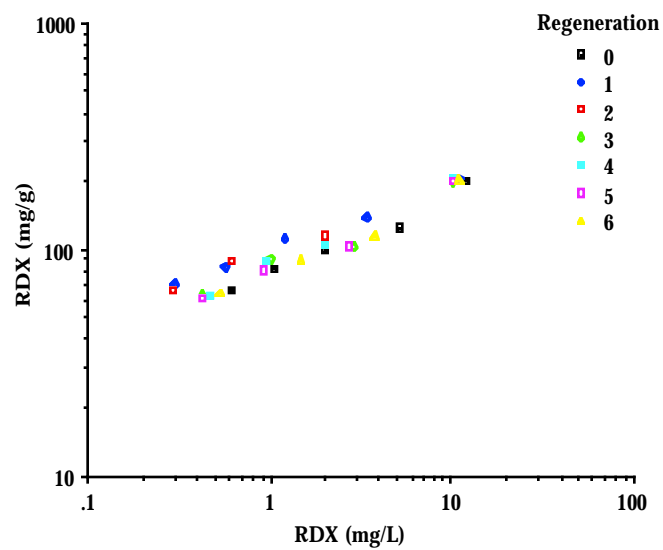


Figure 5. Sorption isotherms for RDX on activated carbon that was regenerated six consecutive times.

Table 1. Concentrations of nutrients required to support the growth of the microbial consortium that degrades RDX and HMX under denitrifying conditions.

	<u>g/L</u>
Phosphate buffer	
K_2HPO_4	5.0
NaH_2PO_4	2.8
Nitrate	
KNO_3	1.6
Ca, Mg, NH_4	
$CaCl_2 \cdot 2H_2O$	0.04
$MgCl_2 \cdot H_2O$	0.10
NH_4Cl	0.20
Ethanol (C_2H_5OH)	25.0
Sodium sulfite (Na_2SO_3)	0.02
	<u>mg/L</u>
Trace Minerals	
$FeCl_3$	3.9
$MnCl_2$	0.95
$ZnCl_2$	0.66
$CoCl_2 \cdot 6H_2O$	0.58
$CuCl_2 \cdot 2H_2O$	0.30
$Na_2MoO_4 \cdot 2H_2O$	0.46
$Na_2B_4O_7 \cdot 10H_2O$	0.24

Table 2. Composition of the off-gas generated by the pilot-scale treatment system that is being used to degrade RDX and HMX.

<u>Gaseous constituent</u>	<u>Composition (%)</u>
N ₂	98.48
O ₂	0.45
C ₂ H ₅ OH	0.38
CO ₂	0.28
H ₂	0.11
N ₂ O	ND ^a
CO	ND ^a

^a Not detected.

Technical Information Department • Lawrence Livermore National Laboratory
University of California • Livermore, California 94551

